

May 26, 1936.

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Filed April 3, 1935

2 Sheets-Sheet 1

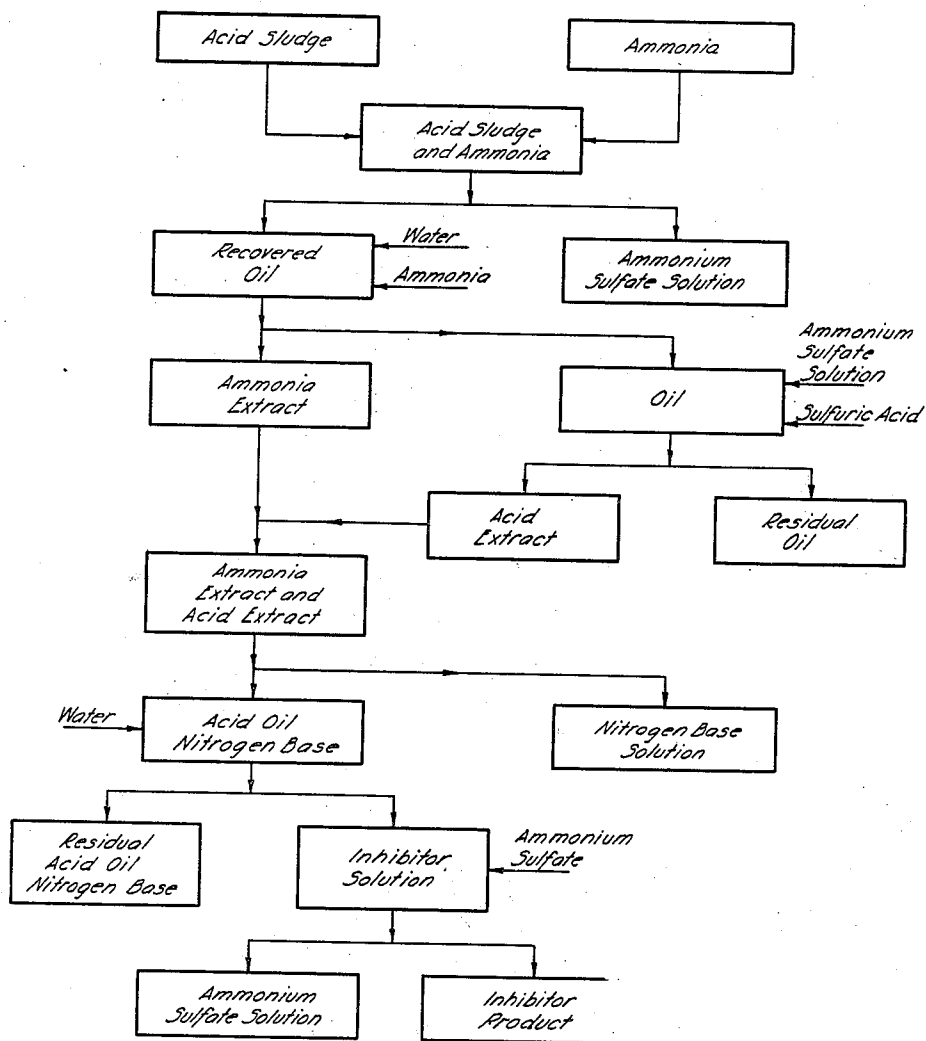


FIG. I.

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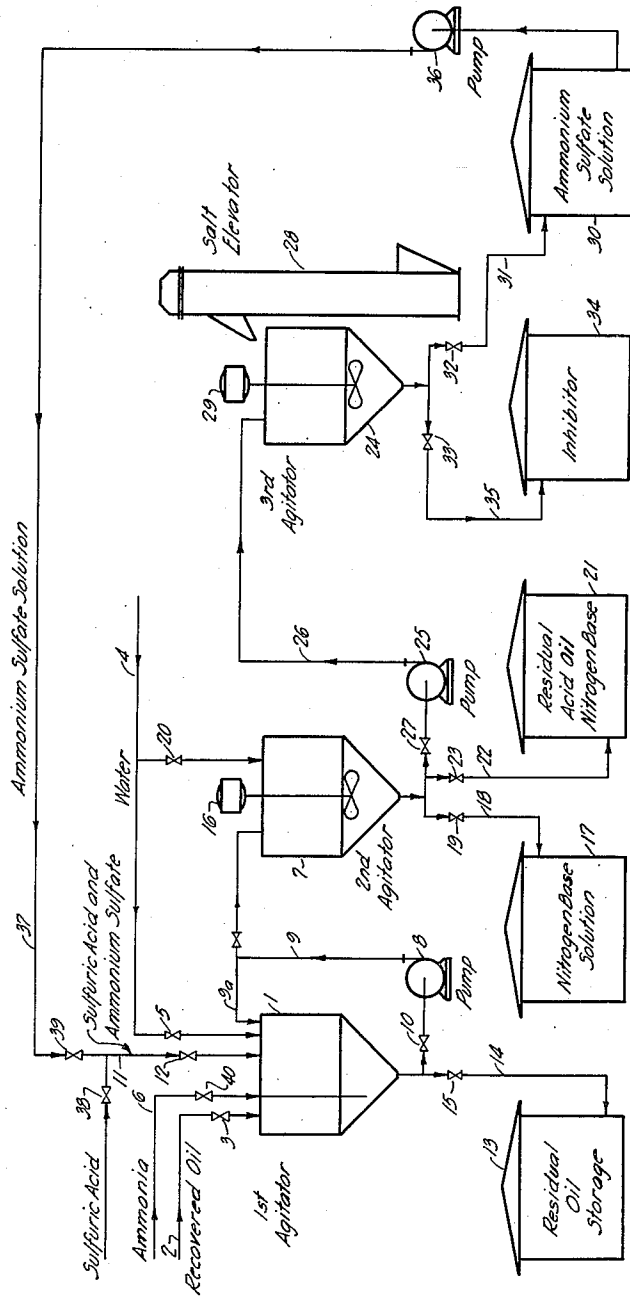


FIG. I.

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# UNITED STATES PATENT OFFICE

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## PROCESS FOR THE PREPARATION OF INHIBITORS

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Application April 3, 1935, Serial No. 14,544

9 Claims. (Cl. 148--8.1)

This invention relates to agents for the prevention of the corrosion which occurs upon the surface of metals when removing undesirable films as in the pickling of steel.

When an article made of a material such as steel is heat processed or is subjected to a prolonged atmospheric exposure, undesirable oxide films form on the surface of the article. Those films are known respectively as mill-scale and rust and usually consist of various oxides of iron. It is desirable to remove these films prior to galvanizing or other finishing process, and for this purpose the article is subjected to a treatment known as "pickling". The pickling operation usually comprises placing the article in a tank or vat containing dilute sulfuric acid. To facilitate the action the acid is usually hot. The acid acts upon the mill-scale and rust converting it into the sulfate. However, the acid also acts upon the metal so that considerable metal may be lost before all the mill-scale and rust is removed from all parts of the article being treated. A considerable waste of acid also results.

Various substances have been proposed for adding to the pickling bath so that the action of the acid will be limited to the mill-scale and rust. These substances have been termed "inhibitors" since they greatly reduce the action of the acid upon the bare metal while at the same time only slightly reducing the action of the acid upon the oxide film. Among the many inhibitors used may be mentioned acid wastes resulting from the treatment of coal tar or petroleum distillates. These are known as acid sludges and many of them contain nitrogen bases.

There are several disadvantages in employing these materials as inhibitors. Due to the insolubility of part of the inhibitor in the pickling bath a scum is often formed on the surface of the acid. This scum adheres to the articles being taken out of the bath, besides sticking to the sides of the pickling bath. The existing inhibitors produced from acid sludge have a most disagreeable odor often so obnoxious as to entirely prevent their use.

It is an object of our invention to devise a process for producing inhibitor from petroleum acid sludges having superior inhibiting properties to those heretofore produced. It is another object to devise a process whereby an inhibitor having no disagreeable odor may be produced from acid sludge. A further object is to produce an inhibitor from petroleum sludges which is completely soluble in the pickling bath. A still further object is to prepare an intermediate for the preparation of organic compounds. The other objects of our invention will be apparent to those skilled in the art from the following detailed description of a preferred form of our invention

throughout which reference is made to the accompanying drawings of which:—

Fig. I is a chart of the process steps involved. Fig. II is a diagrammatic flow sheet of apparatus suitable for carrying out the process.

Referring to Figure I acid sludge resulting from the treatment of petroleum distillates is first neutralized with ammonia preferably in a saturated solution of ammonium sulfate. As a result the sulfuric acid in the acid sludge is neutralized producing ammonium sulfate. Certain organic sulfates present in the acid sludge are also acted upon by the ammonia forming ammonium sulfate and releasing organic oily material. This latter material together with other oil originally present in the acid sludge collects on the surface of the aqueous liquid from which it is removed. Throughout the rest of this specification and claims, we refer to this separated oily material resulting from the neutralization of acid sludge as "recovered oil".

If necessary, the "recovered oil" is heated to a sufficiently high temperature so that its fluidity is sufficiently increased to facilitate further treatment. Thereafter an aqueous solution of ammonia is added to the "recovered oil" to produce free ammonia in the container in such amounts that a small excess of ammonia exists in the mixture. After sufficient time has elapsed the liquid will separate into two layers. The aqueous layer of ammonia extract is drained off to a second container. The effect of this ammonia treatment is to extract certain organic material which we have called acid oil. The remaining oily material in the container is next treated with sulfuric acid and preferably ammonium sulfate. This treatment extracts basic compounds from the oily material. In our work we have preferred to use ammonia, sulfuric acid and ammonium sulfate as treating agents but the process may be executed equally well with other alkalis, acids and alkaline salts respectively. The basic compounds extracted from the oil are mostly nitrogen compounds and will be referred to hereafter as nitrogen bases. It will thus be seen that we now have an ammonia extract containing acid oil and an acid extract containing nitrogen bases. The two extracts are next mixed one with the other. As a result of this mixing the acid oil and nitrogen bases become released from their carriers and combine with one another forming a layer which we have called "acid oil nitrogen base". This product is removed and diluted with water resulting in further stratification of the material. The upper layer called "inhibitor solution" is separated from the other liquor called "residual acid oil nitrogen base". Ammonium sulfate either as a solid salt or as concentrated aqueous solution is added to the inhibitor solution and has the effect of concentrat-

ing the inhibitor by its salting out effect. Other salts may be used for the same purpose. The finished product is removed from the surface of the tank.

5 This product is soluble in sulfuric acid, possesses no disagreeable smell and has good inhibiting properties. Instead of concentrating the inhibitor from the "inhibitor solution" by adding ammonium sulfate as above mentioned, the "inhibitor solution" could be used directly as such, however, its inhibiting qualities will be proportional to the concentration of the finished inhibitor in the solution.

Referring to Fig. II which shows in elevation apparatus suitable for carrying out our process, a required amount of "recovered oil" produced by neutralizing acid sludge with ammonia is introduced into the first agitator (1) from pipe (2) controlled by valve (3). Water is then run into the agitator (1) from pipe (4) controlled by valve (5). Thereafter, amounts of ammonia gas are passed into the agitator through pipe (6) which extends to the bottom of said agitator (1). The ammonia flow is controlled by a valve (40). The ammonia gas entering stirs the mixture so that a mechanical stirrer can be dispensed with. During the addition of ammonia gas the contents of the agitator are circulated by pump (8) through lines (9) and (9a). Instead of using ammonia gas and water, we may, of course, use an aqueous ammonia solution of desired concentration. After sufficient ammonia has been passed in so that the resulting mixture is slightly ammoniacal, the ammonia valve is closed. After a short period a layer of ammonia extract will gravitate to the bottom of the agitator (1). This extract is pumped from the first agitator (1) to the second agitator (7) by means of pump (8) and line (9) controlled by valve (10). After the ammonia extract has been drawn off the valve (10) is closed. To the oily material now remaining in the first agitator amounts of sulfuric acid and ammonium sulfate solution from line (11) controlled by valve (12) are added and the contents of the agitator are circulated by means of pump (8) through lines (9) and (9a). As a result a layer of acid extract containing nitrogen bases settles to the bottom of the vessel. This acid extract is pumped to the second agitator (7) through line (9) by opening valve (10) and starting up pump (8). After the acid extract has been transferred to the second agitator, the valve (10) is closed and the remaining oily material is run to storage tank (13) through pipe (14) by opening valve (15). This material can be used as fuel under boilers.

The ammonia extract and the acid extract are next mixed in the second agitator (7) by means of a stirrer (16). As a result of this admixture the acid oil of the ammonia extract combines with some of the nitrogen bases of the sulfuric acid extract forming a layer of "acid oil nitrogen base" material on a layer of nitrogen bases dissolved in a sulfuric acid and ammonium sulfate solution. (This latter we have called "nitrogen base solution".) The nitrogen base solution is withdrawn from the second agitator (7) to storage tank (17) by means of pipe (18) by opening valve (19). This nitrogen base solution can be used as a source of nitrogen bases by subsequent treating. To "acid oil nitrogen base" material remaining in the second agitator is added water from line (4) by opening valve (20). After sufficient water has been run in, the valve (20) is closed and the contents of the agitator mixed by means of stirrer (16). After thorough mixing

the material separates into two layers upon standing. The lower layer called "residual acid oil nitrogen base" is run to a storage tank (21) through pipe (22) by opening valve (23). The valve (23) is closed after all the lower layer has been withdrawn and the upper layer called "inhibitor solution" is pumped into the third agitator (24) by means of pump (25) by means of pipe (26) by opening valve (27). An amount of solid ammonium sulfate is then dumped into this third agitator (24) from salt elevator (28). The stirrer (29) is next operated to cause the contents to be thoroughly mixed. After sufficient time for settling has elapsed the inhibitor rises to the top of the remaining liquor, which liquor consists of ammonium sulfate solution. This ammonium sulfate solution is then drawn off to a storage tank (30) by pipe (31) by opening valve (32). When the ammonium sulfate solution has all run off, valve (32) is closed and valve (33) is opened allowing the inhibitor to run to its storage tank (34) by pipe (35).

The ammonium sulfate solution in tank (30) can be mixed with sulfuric acid in the necessary proportions for introducing into the first agitator (1) by pumping the same in controlled amounts into line (11) by means of pump (36) and line (37). The proportion of ammonium sulfate to sulfuric acid can be controlled by regulation of valves (38) and (39).

The inhibitor as produced by our process is soluble in dilute sulfuric acid, has no unpleasant smell and has been found to have inhibiting properties equal to "Rodine No. 110" which has the following analysis:

	Per cent
Symmetrical 2-methyl phenyl thiourea.....	27.5
Sodium chloride.....	67.5
Glue.....	5.0

Our inhibitor is used in the same manner as "Rodine No. 110".

The usual practice in the pickling of steel plates for the manufacture of tin plates is to make a pickling bath of desired sulfuric acid concentration, mix in the necessary quantity of inhibitor and dip the plates into the bath in batches. As the acid is consumed, more 66° Bé. sulfuric acid and inhibitor are added to maintain the concentration within the desired limits.

As an example of commercial test with our product the following is given:

Total H <sub>2</sub> SO <sub>4</sub> 66° Bé. used.....	4840 lbs.
Acid concentration of bath.....	7% H <sub>2</sub> SO <sub>4</sub>
Inhibitor used—4550 cc.....	9.60 lbs.
Steel pickled.....	66.07 long tons
Amount of inhibitor used per long ton of steel treated.....	.145 lb.

As a specific example of operating conditions of our process the following example is given: The "recovered oil" was obtained by neutralizing acid sludge (resulting from the treatment of pressure distillate, a cracked petroleum product) with ammonia. The "recovered oil" at a temperature of approximately 80° C. was mixed with approximately one-seventh its volume of water at the same temperature to which 2% of its weight of gaseous ammonia was added during the mixing of the liquids. After mixing and settling the ammonia extract was separated from the oil. A hot, nearly saturated solution of ammonium sulfate and 67% sulfuric acid was next added to the oil, the ratio of the volume of ammonium sulfate solution to sulfuric acid being kept at

about 6:1. Approximately 72.5 gr. of sulfuric acid were required to extract the nitrogen bases from a liter of "recovered oil". The resulting acid extract after settling was removed and mixed with the ammonia extract. Upon standing an aqueous solution of nitrogen bases separated from the "acid oil nitrogen base". Thereafter the "acid oil nitrogen base" was mixed with twice the amount of water which caused a separation in two layers. The upper layer was mixed with enough solid ammonium sulfate to render the whole approximately saturated. The inhibitor product was separated from the ammonium sulfate solution by skimming.

Our product besides being an excellent inhibitor for the pickling of steel has been found to have value as an insecticide.

It should be borne in mind that the above is by way of example and that the exact operating conditions will vary with different sludges. It is not intended that the specific details be regarded as limitations upon the scope of the invention which is set forth in the appended claims.

We claim as our invention:

1. Process for the manufacture of steel pickling inhibitor from petroleum acid sludge comprising neutralizing the acid content of said sludge, adding alkali to the oily layer produced, removing the resulting alkaline extract, adding acid and alkaline salt to the remaining oil, removing the acid extract produced, mixing said alkaline extract with said acid extract, removing the resulting acid oil nitrogen base, hydrolyzing said acid oil nitrogen base whereby a layer of inhibitor solution is produced, thereafter separating inhibitor from said solution by means of a suitable salt.

2. Process for the manufacture of steel pickling inhibitor from petroleum acid sludge comprising neutralizing the acid content of said sludge, adding ammonia to the oily layer produced, removing the resulting ammonia extract, adding sulfuric acid and ammonium sulfate to the remaining oil, removing the acid extract produced, mixing said ammonia extract with said acid extract, removing the resulting acid oil nitrogen base, hydrolyzing said acid oil nitrogen base whereby a layer of inhibitor solution is produced, thereafter separating inhibitor from said solution by means of ammonium sulfate.

3. Process for the manufacture of steel pickling inhibitor from petroleum acid sludge comprising neutralizing the acid content of said sludge, adding ammonia to the oil layer produced, removing the resulting ammonia extract, adding sulfuric acid and ammonium sulfate to the remaining oil, removing the acid extract produced, mixing said ammonia extract with said acid extract, removing the resulting acid oil nitrogen base, hydrolyzing said acid oil nitrogen base whereby a layer of inhibitor solution is produced, thereafter separating inhibitor from said solution.

4. Process for the manufacture of steel pickling inhibitor from petroleum acid sludge comprising neutralizing the acid content of said sludge with ammonia, separating the oily material produced, adding ammonia to said oily material, removing the resulting ammonia extract, adding sulfuric acid to the remaining oil, removing the acid extract produced, mixing said ammonia extract with said acid extract, removing the resulting acid oil nitrogen base, hydrolyzing said acid oil nitrogen base whereby a layer of inhibitor solution is produced, thereafter separating inhibitor from said solution by adding ammonium sulfate.

5. Process for the manufacture of steel pickling inhibitor from petroleum acid sludge comprising neutralizing the acid content of said sludge with ammonia, separating the oily material produced, adding ammonia to said oily material whereby an ammonia extract is produced, separating the ammonia extract from the remaining oil, adding sulfuric acid to the remaining oil, whereby an acid extract is produced, separating the acid extract from the remaining residual oil, adding said acid extract to said ammonia extract whereby a layer of acid oil nitrogen base material is produced, removing the acid oil nitrogen base material, hydrolyzing the same whereby a layer of inhibitor solution is formed, removing the inhibitor solution and separating inhibitor therefrom by the addition of a concentrated ammonium sulfate solution.

6. Process for the manufacture of steel pickling inhibitor from petroleum acid sludge comprising neutralizing the acid content of said sludge with ammonia, removing the resulting oily layer, adding ammonia to this oily layer, removing the resulting ammonia extract, adding ammonium sulfate and sulfuric acid in the proportion of six parts ammonium sulfate to one part sulfuric acid to the remaining oil, removing the resulting acid extract, adding the acid extract to the ammonia extract whereby a layer of acid oil nitrogen base material is produced, hydrolyzing said acid oil nitrogen base material whereby a layer of inhibitor solution is produced, thereafter separating inhibitor from said solution.

7. Process for the manufacture of pickling inhibitor from petroleum acid sludge comprising neutralizing the acid content of said sludge with ammonia, extracting acid oil material from the oily material produced by said neutralization, then extracting nitrogen base material from said oily material, adding said acid oil material to said nitrogen base material whereby an acid oil nitrogen base is produced, adding amounts of water to said acid oil nitrogen base, separating the upper layer of liquid produced and adding solid ammonium sulfate to said upper layer, to separate the inhibitor.

8. The herein described pickling inhibitor obtained by neutralizing the acid content of petroleum acid sludge with ammonia, separating the oily material produced, adding ammonia to said oily material, removing the resulting ammonia extract, adding sulfuric acid to the remaining oil, removing the acid extract produced, mixing said ammonia extract with said acid extract, removing the resulting acid oil nitrogen base, hydrolyzing said acid oil nitrogen base whereby a layer of inhibitor solution is produced, and separating said inhibitor from said solution by the addition of ammonium sulfate.

9. Process for the manufacture of steel pickling inhibitor from petroleum acid sludge comprising substantially neutralizing the acid content of said sludge, adding a base to the oily layer produced removing the resulting basic extract, adding acid and a salt of the alkali earth metals including ammonium, removing the acid extract produced, mixing said basic extract with said acid extract, removing the resulting acid oil nitrogen base, hydrolyzing said acid oil nitrogen base whereby a layer of inhibitor solution is produced and thereafter separating inhibitor from said solution by means of a suitable salt.

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